

Spatial Trends of Cadmium and Zinc Concentrations in Water and Enrichments in Surficial Sediments Within Nyanza (Winam) Gulf of Lake Victoria (East Africa)

ABSTRACT

Metal pollution contributes significantly to the environmental degradation of lake ecosystems. The study evaluated the spatial trends in cadmium and zinc concentrations in surface water, un-fractionated and the <math><63\mu\text{m}</math> grain size fraction (silt and clay) of surficial sediments within Nyanza Gulf, from lake monitoring stations in 2010 and 2012 surveys. Significantly higher Zn total concentrations were found in surface lake water compared to earlier surveys, but cadmium levels were low and not detectable as in previous studies. Variable contents of Zn and Cd were found in un-fractionated and finer sediment fractions. "Much higher sediment Cd contents were found in 2010 compared to other surveys. Major areas under river and urban influences recorded much higher sediment Cd contents than offshore sediments. However, there were no significant differences between Cd and Zn contents between the gulf and main lake zones. Cd sediment enrichment factors were highly variable compared to Zn, which showed a more uniform trend in most of the gulf areas, but Cd sediment enrichment factors appear to increase when compared to previous data. The spatial distribution of Cd and Zn in the surficial sediments show unpolluted to moderate pollution levels, according to geo-accumulation index. Only 4% of Zn samples exceeded the sediment quality threshold effect concentration (TEC) values, but all were below the mid-range effect values. Cadmium is a recognized toxicant and there are potential ecological concerns regarding the variable sediment Cd contents since it has been found previously in bioavailable forms in surficial sediments and 2% of the samples contained Cd (un-fractionated sediment) above the threshold effect concentration during the 2012 survey compared to 51 % in 2010, but none exceeded the severe effect levels". Continuous monitoring of priority heavy metals is of relevance on the understanding of potential long-term ecological impacts to the lake ecosystem.

Keywords: *Lake Victoria, heavy metals, monitoring, aquatic pollution; surficial sediment quality*

1. INTRODUCTION

Metals and metalloids are a great concern in lakes utilized for different human activities, and acting as principal waste receptors and dilutants. Domestic wastewater is the largest single source of heavy metals discharged to the environment in effluents or sewage sludges which generally contain elevated levels of copper, lead zinc, cadmium and silver (Forstner and Wittman, 1983). Stormwater runoff in urban areas contains relatively high levels of heavy metals such as Cu, Pb and Zn, together with bacteria, nutrients and a high BOD. The metals will be associated to a greater extent with particulates, which means that metal concentrations in receiving lakes may be localized, unless the suspended particulates are transported extensively, for example in some shallow lakes (Poolman and Danek, 1988). "In most cases,

bioavailability and toxicity effects will vary depending on the water conditions and metal speciation. Cadmium is a non-essential heavy metal. The International Agency for Research on Cancer (IARC) classifies cadmium in Group 1: carcinogenic to humans and the US Environmental Protection Agency (EPA) has determined that cadmium is a probable human carcinogen by inhalation (UNEP, 2010). Cadmium is a soft metal that resembles zinc in (many of Delete)its physical and chemical properties. However, it is much less abundant in the Earth's crust than zinc. It is found most commonly in ores of zinc. Most cadmium is obtained as a by-product from zinc refinement. A popular use of cadmium compounds Xas coloring agents. The two compounds most commonly used are cadmium sulfide (CdS) and cadmium selenide (CdSe). Ni-Cd is used in the production of batteries. The only important ore of cadmium is greenockite, or cadmium sulfide” (Cadmium, 2015). Wastes from these sources also provide important sources of Xbioaccumulative Cd to the environment.

Heavy metals are a concern in lake ecosystems since they are toxic and provide active metal pools for biological uptake from lake water and sediments when in high concentrations. Where potential point sources exist, elevated concentrations can lead to increased bioavailability in the lake ecosystem with adverse ecological impacts. Direct effluent discharges or spills from industrial activities, inadequately treated domestic and urban wastewaters are significant sources from urbanized lakeshore areas and in catchments with a wide range of agricultural, and industrial activities. Some fertilizers are also known to contribute to metal sources in agricultural soils, which reach downstream water bodies through subsurface leaching, river and surface runoff transports, or aerial particulate deposition. Concerns have also been raised on aquaculture related trace metals in marine sediments (Price and Morris, 2013 and Chou et al., 2002), although there were no lake aquaculture activities in the study area during the surveys.

“Cadmium enters aquatic systems through aerial deposition or runoff X accumulates in bed sediments by association with particulate matter, such as organic matter and iron and manganese hydroxides, or by precipitating out of solution with carbonate or sulfide” (Landrum and Robbins, 1990, and Burton, 1992). “In freshwater, the cadmium ion is the predominant dissolved form, while in seawater, chloride dominates” (Wright and Welbourn, 1994). “Much of the cadmium added to aquatic systems accumulates in sediments where it presents a risk to benthic biota and under certain conditions may re-enter the water column. Sediments, therefore, act as an important route of exposure for aquatic organisms. Cadmium may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide, and phosphate” (USEPA, 1999). “Cadmium is readily accumulated by many organisms, particularly by micro-organisms and molluscs in which bioaccumulation factors are in the order of thousands. Soil invertebrates also concentrate cadmium markedly in their tissue. Most organisms show low to moderate concentration factors of less than 100” (IPCS, 1992) Metals are accumulated by filter feeding organisms via water, ingestion of suspended sediments or food. This forms a source for uptake along the aquatic food chain. In the Nyanza gulf Cd and Zn levels are among the trace elements concentrations of interest reported in different environmental compartments and samples (Ongeri et al., 2015, 2009a, 2009b, Ngure et al., 2014, Muinde et al., 2013, Mwamburi 2013, Oyoo-Okoth et al., 2013, 2012a, 2012b, 2012c, Ogoyi et al., 2011, Odum et al., 2011a, 2011b, Adoli et al., 2011, Omwoma et al., 2010, Lalah et al., 2008, Shitsama, 1999, Mwamburi and Oloo, 1996/7, and Onyari and Wandiga, 1989).Also, evaluation of metals in fish endoparasites provided evidence that fish parasites, *Lingulaintestinalis* infection enhance Cd accumulation, but depletes the essential Co in the cyprinid fish *R. argentea*. (Oyoo-Okoth et al., 2012b).

The lake basin and its surrounding highlands are fertile agricultural soils with the northern and southern regions known for gold mining activities. The use of agricultural fertilizers and other agrochemicals are potential sources of heavy metals in soils, which together with other terrestrially derived materials and urban waste disposal, contribute to the metal loading in lake sediments overtime. Cadmium and Zn are geochemically associated, and in lake basins known to be enriched with minerals, such as the L. Victoria Kenya basin, leaching and mine wastes can result in excessive levels in surface and underground waters and river-lake sediments. Also, long-term use of chemicals in aquaculture activities can cause enrichments of metals in sediments, from the used of antifoulants, and wasted or un-utilized feeds. Therefore, monitoring the lake sediments, which act as secondary sources of metal contaminants to the above water column, can indicate Cd and Zn bioavailability and potential ecological risks to aquatic habitats.

Several investigations and reports on the metal contaminants within

Lake Victoria (East Africa) have been conducted through different projects and studies. This study was part of the monitoring surveys of these trace elements within the Nyanza Gulf, with more details on the sedimentary environment regarding metal toxicants and evaluating of their potential ecological effects. Sediment quality guidelines were used to make quality evaluations for the protection of aquatic biota. Therefore the study is partly to characterize spatial trends in contamination of Cd and Zn, and provide a comparison with data from previous surveys to assess any changes in environmental quality. This forms part of the surveys which are designed to monitor and assist in tracing possible sources and vectors of contamination.

2. MATERIALS AND METHODS

2.1 Study area

Lake Victoria, East Africa (Fig. 1), is the second largest freshwater lake in the world after Lake Superior in the USA, and the largest African inland lake also valued for its commercial fishery and rich biodiversity. "It has a surface area of about 68,800 km², a mean and maximum depth of 40m and 80m respectively, and a water volume of about 2,760 km³. Rain and river inflow are the main water inputs into the lake, with an estimated flushing time of 140 years and residence time of 23 years" (Bootsma and Hecky, 1993; Wellcome, 1972). It loses water mainly through evaporation and the Nile River. The main lake catchment area is about 194,000 km².

The oldest supracrustal rocks in Kenya are the Archean Nyanzian meta-volcanic and the Kavirondian meta-sediments (Opiyo-Akech, 2013, Opiyo-Akech et al., 1999, Ngecu and Gaciri, 1995). "These are in most parts separated from the Archean rocks by the Tertiary volcanic associated with the East African rift system" (Opiyo-Akech, 2013). "The Nyanzian group at the base is composed of tholeiitic basalts, calc-alkaline dacites and rhyolites" (Opiyo-Akech et al., 1999). The group is unconformably overlain by the Kavirondian group (Ngecu and Gaciri, 1995, Mathu and Davies, 1996). The most productive gold deposits in Tanzania and southwestern Kenya (Condie, 1981, and Kuehn et al., 1990) are in the Nyanzian greenstone belts (2,700Ma) and the Ubendian system (2000Ma). "Gold mineralization occurs in proximal facies tuff and iron formation, and oblique of the semi-conformable quartz veins". (Ichangi and Maclean, 1991). "Artisanal activities in Au processing have been of interest in the Archean Nyanzaian greenstone belt areas around Lake Victoria basin due to the potential use of Hg.

Lake Victoria bottom is mainly covered by a thick layer of organic mud, but with patches of hard substrate, sand and shingle or rock” (Scholtz et al., 1990). Water hyacinth (Aloo et al., 2013) and eutrophic conditions (Sitoki et al. 2010, Mugidde et al., 2005, Lungaiya et al., 2001, and Hecky et al., 1994) are also a common phenomenon in the lake, linked to ecological changes in the lake.

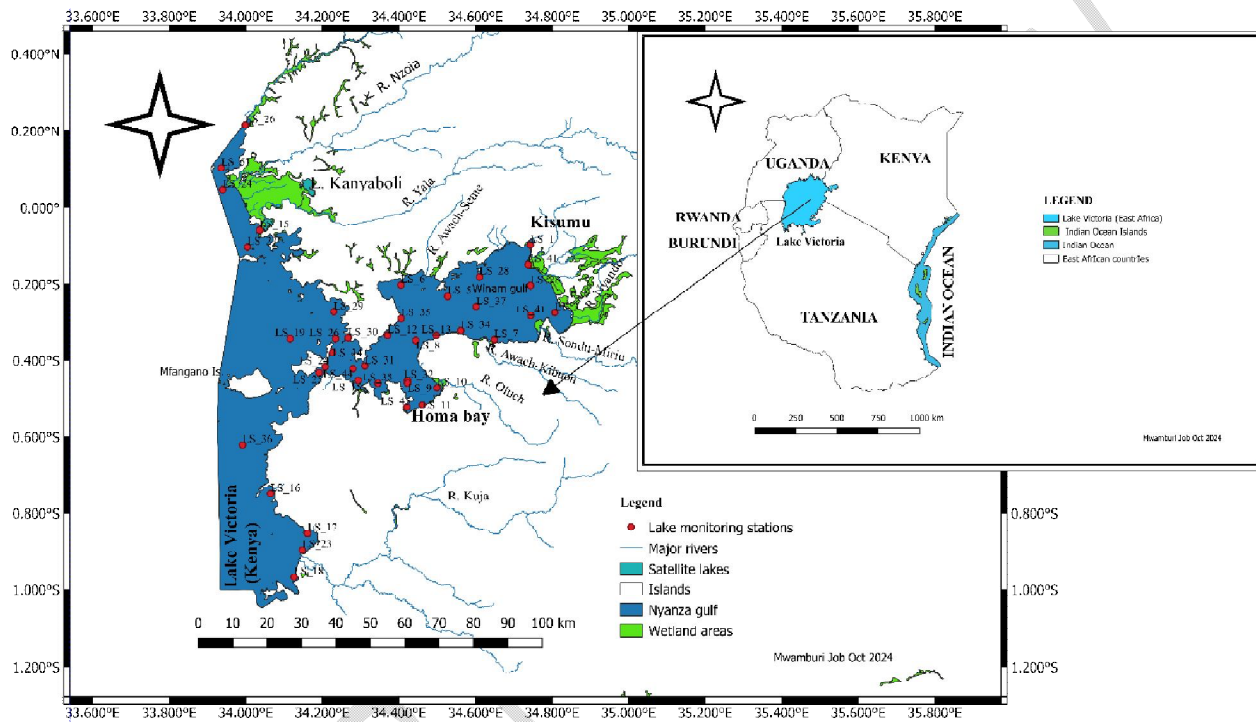


Fig 1. A map of the eastern gulf (Winam or Nyanza Gulf) of Lake Victoria (East Africa), showing the sampling stations.

Fish inhabiting shallow waters are also at risk from periodic upwelling of hypoxic waters (Aloo et al., 2013).

“Nyanza gulf, the eastern section of the main lake forming the Kenyan portion, consists of a small open lake section and the Winam gulf. The Winam gulf is relatively shallow, but deepens westwards, and its catchment area is dissected by several rivers and tributaries. Rivers Nyando, Sondu-Miriu, Awach, Nzoia, Yala, Sio and Kuja are major inflowing rivers. The several inflowing river mouth areas, shallow inner bays and island shore are important habitats for fish and aquatic organisms. The shallow (less than 5m deep) inshore zone has been known to be the main area of artisanal fisheries” (Balirwa et al., 2005), Critical habitats in the Lake Victoria basin include shallow inshore areas, rocky areas of the lake, sheltered bays and vegetated shorelines. The lakeshore wetlands in flowing

“Rivers and streams, the different types of bottom (rocky, sandy, muddy) and depth are among features that account for the patchy distribution and variable abundance of fish species in the lake” (Balirwa et al., 2005).

2.2 Sampling

“The monitoring survey was conducted in June 2012 by maintaining as close as possible the same (Global Positioning System, GPS coordinates) marked sampling stations (Figure 1) used during the 2010 survey to ensure they coincide with sites where much of the historical data sets were derived from. Some of the physico-chemical conditions of bottom water (water overlying the bottom sediments) were determined insitu using a CTD-90 M sensor (Sea & Sun Technology) and data downloaded into a computer using Windows based standard data acquisition software.

In terms of the influence of inflowing rivers, the Kenyan portion can be distinguished as follows: Inner shallow bays, Zone I: The inner shallow bay with influence from major rivers Kibos-Nyamasaria, Nyando, Awach and Sondu-Miriu, with average water depths of about 5m. The rivers are located in the southeastern zone and drain agricultural and urban areas.”

Sites: LS_1 (Kisumu Pier); LS_2 (Maboko Is.); LS_3 (Off Nyando river mouth); LS_4 (Off SonduMiriu); LS_6 (Asembo bay); LS_7 (Off Awach River mouth); LS_8 (Gingra rock); LS_34 (Mitimbili); LS_35 (AchiengOnoko); LS_13 (Balarawi); LS_28 (Off Kibos RM); LS_5 (Off Ndere Isl.). Middle Deeper Zone II: The middle deep gulf zone with deep waters and connected to open waters; Urban developments and agricultural zones are on both sides, with R. Oluch drainage entering the lake near HomaBay. Sites: LS_9 (Soklo); LS_10 (Oluch RM); LS_11 (Homabay); LS_12 (Kopiata); LS_14 (Utajo); LS_15 (Luanda Gembe); LS_24 (Mbita East); LS_37 (Mid gulf); LS_33 (MirundaBay); LS_30 (Luanda Kotieno); LS_26 (Rusinga channel); LS_31 (Madundu); LS_32 (Kowuor).Offshore and open lake Zone III (south and north): The offshore open lake waters with shallow nearshore margins, are exposed to heavy wind and wave action. This section forms a connection with the catchment through rivers Kuja in the southern zone and rivers Sio, Nzoia and Yala in the northern zone. These are extensive rivers draining expanses and rich agricultural areas. Both the middle and inshore zones of the gulf are often covered by water hyacinth. Sites: Southern section: LS_16 (Matara bay); LS_17 (Sori-Karungu); LS_18 (MuhuruBay); LS_25 (Mbita west); LS_36 (Remba); Northern section LS_19 (Bridge Is.); LS_20 (Off Yala RM); LS_21 (Off Nzoia RM); LS_22 (Off Sio RM); LS_23 (Off Kuja RM);

2.2.1 Physico-chemical parameters

Surface water temperature, conductivity, dissolved oxygen and pH were measured insitu using a multiparameter (Hydrolab) instrument. Water transparency and turbidity were measured using a Secchi disk and HachTurbidimeter (2100P) respectively. All the meters were calibrated in the laboratory and in the field according to the specified conditions in the manufacturer's manuals. The total alkalinity and total hardness were determined in the field by acid titration methods, as outlined in APHA (1985), immediately after sample collection.

2.2.2 Water

Water samples were collected below the water surface using a water sampler. Samples for determination of dissolved metals were transferred into pre-cleaned 500ml polyethylene bottles. The water samples were preserved with concentrated Nitric acid (analytical grade, 70% w/w) in pre-cleaned polyethylene bottles and digested according to APHA (1985), using concentrated Nitric acid (analytical grade, 70% w/w) in the laboratory. Total metal acid blank samples were digested X similarlyX and analyzed for the metal.

2.2.3 Bottom sediments

Surficial sediments were collected using a pre-cleaned polar grab sampler. The innermost portions of sediments were used for gravimetric determinations and trace metal chemical analysis, to avoid portions in contact with the grab sampler. The field samples were kept frozen in pre-cleaned high density polythene bags in the field, before initial sample preparation in the laboratory. The sediments were characterized by the determination of the percentage of water, carbonate and organic matter contents. The water content was determined by oven – drying about 5.0g of the wet sediment at 105 °C for 6 hours and to constant weight. About 1.0g of the dry sediment was used to determine the carbonate and organic matter contents. The percentage Loss on Ignition (% L.O.I) was also determined by heating about 1.0g of the dry sediment at 550 °C (Hakanson and Jansson, 1983) in a furnace and determining the weight loss. Sediment bulk density (g/cm³) was also determined according to calculation of (Hakanson and Jansson, 1983). All determinations were made in triplicates. To ensure quality of data, all dried samples were cooled in a desiccator and gravimetric measurements were made inside the laboratory using sensitive analytical balances. This ensured all possible contamination from the air was avoided.

About 1.0 g of the sediment was digested with 10mL (3:1 v/v ratio) of conc. HCl - HNO₃ mixture at 90 °C for 60 minutes. Acid blanks together with the digested sample solutions were diluted to mark in 50ml volumetric flasks. All glassware used in the extractions was soaked in 10% HNO₃ v/v, and rinsed with deionized water. All reagents used were of analytical grade to check for possible contamination, and blanks were carried through the same procedures. Replicates were included in all analyses.

2.3 Chemical and Statistical Analysis

Elemental concentrations in both samples were determined using flame and graphite Atomic Absorption Spectrophotometer (Varian Techtron Spectra AA-10, Varian Techtron PTY Ltd. Varian Associates Inc.), according to the manufacturers conditions with appropriate standard solutions. Statistical Analysis was performed using the SPSS (Ver. 10.0) and Statistical (Ver. 4.3) packages. Significant Pearson's (r) correlation coefficients were determined and mean metal concentration was compared using one way analysis of variance, ANOVA at a 5% significance level. Instrumental analysis of Cd and Zn was done after the digestion of samples in the Mines and geological laboratories in Nairobi. Samples Cd samples were also submitted to another National laboratory (KEPHIS, Kenya Plant Health Inspectorate laboratory, Nairobi) for quality control and assurance. These laboratories have high standards for metal analysis and all procedures for QC/QA were observed to avoid contamination of sediment samples. Although recovery studies were not conducted, all samples were analyzed together with batches of blank samples, to check for any contamination.

3. RESULTS

The characteristic conditions of waters of the Nyanza Gulf are as shown in Table 1, with slight differences between the gulf and main lake water, and between the surface and bottom waters. Surface water in offshore and deeper areas is more clear than in nearshore areas. Water transparency increases towards the offshore and open waters, whereas the conductivity decreases towards the main lake.

The total zinc concentration in the surface waters ranged from (nd ???) to 4.0 mg/L (Fig. 2), with a mean of 1.97±0.24mg/L. There was a clear spatial variation in the Zn contents, with most of the concentrations below 2.5mg/L. The total concentrations of Cd in surface lake water were all

below the detection level during 2010 survey, and much lower than the Zn contents in sediments. Figures 3a & 3b show the spatial distribution of Cd and Zn concentration (dry weight basis) in un-fractionated and less than 63µm grain size sediment fraction during 2010 and 2012 and compared to previous concentrations from 1994/5 monthly surveys. In sediments, zinc occurs in much higher contents than Cd. In 2012, the mean Zn (\pm sd) concentrations in surficial sediments were 114.65 ± 45.9 µg/g (un-fractionated sediment) and 82.7 ± 31.95 µg/g (<63µm grain size fraction), with much lower .

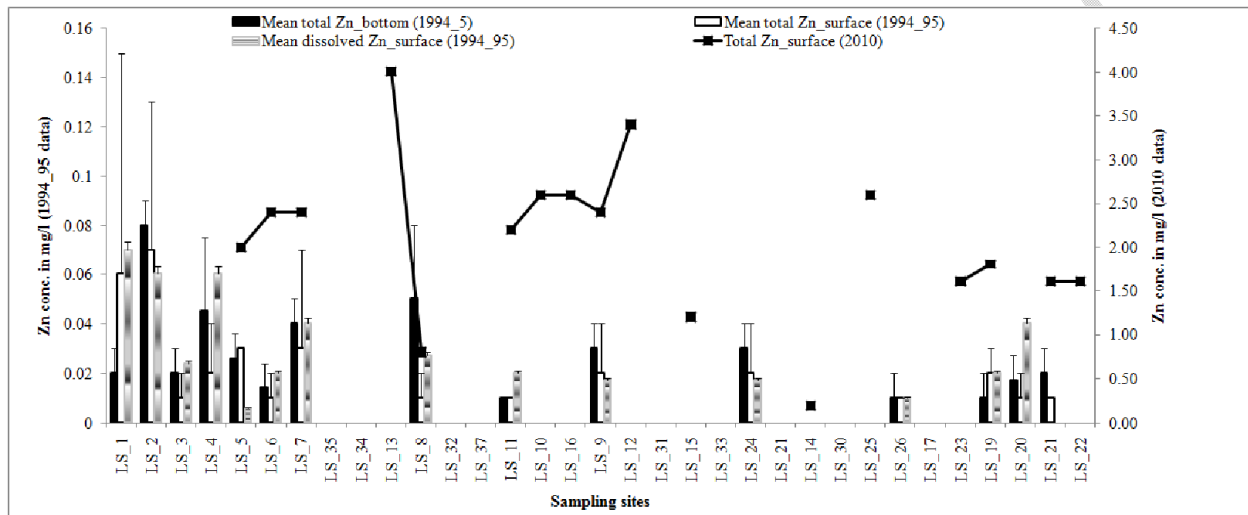


Fig 2. Dissolved and total Zn concentration in surface and bottom waters (2010, 1994/1995 data) of the Nyanza gulf.

contents in 2010 (66.7 ± 36.4 µg/g in un-fractionated sediment and in finer sediments). Cd was below detection level in most of the finer sediments, and concentrations ranged from (nd???) to 0.75 µg/g (2012, with a mean of 0.56 µg/g) and (nd- ????) 5.6 µg/g (2010, with a mean of 1.02 ± 1.73 µg/g). However, in the un-fractionated sediments mean contents of Cd ranged from nd to 0.932 ± 0.413 µg/g (2012) and a range of nd???- 9.6 µg/g in 2010 (with a mean of 1.70 ± 1.70 µg/g). The overall mean (\pm sd) Cd was 0.199 ± 0.23 µg/g in un-fractionated sediments in 2012.

The single highest Cd contents in 2010 were at sites LS_5, 7, 10, 9, 16, 22 & 24, whereas in 2012, peak concentrations occurred at sites LS_35, 19 & 23. The concentrations of Zn were less variable, with distinct maximum values at sites LS_3, 8, 1 & 19 in 2010 and LS_13, 20, 35, 16 & 17. Most of the Zn and Cd were found contained in the un-fractionated sediment and not the <63µm grain size fraction, as expected. However, more Cd and Zn concentrations were found in the finer sediments at sites LS_9, 16, 17, 22, & 25 (Cd) and LS_1, 5, 9, 19, 8, (Zn) in 2010. In 2012, higher contents in the finer sediments were found in sites, LS_10, 14, 23, 24, 8, 9 (Zn) and LS_23, 16, 15 & 19 (Cd). The spatial concentrations of Cd and Zn in the different water depth ranges sampled and zones within the WinamGulf and main lake are shown in Tables 2 – 5. There were no significant differences in mean Cd in the different zones and depth of the sampling site in 2010, but significant differences were found for 2012 data, for means of the sampling ranges only. The mean Zn concentrations did not show any significant differences between zones and water sampling depths, X even when means in the gulf were compared with

those in the main lake. Levels of Zn found in two sediment portions, and data from 2010 and 2012 in the un-fractionated sediment were also found to be significantly different (between years, $F_{1,48}$; $P=.05$; between sediment portions $F_{1,43}$; $P=0.05$) and similar for the finer sediments. Major urban sites contained much higher mean Cd contents in un-fractionated sediment compared to offshore and river influenced areas in both years when all the gulf and main lake data were combined, although not statistically significant.

The Pearson correlation coefficients (r) between the Zn, Cd, % organic matter, % carbonate and %H₂O in surficial sediments were low (Table 6). All zinc and cadmium contents (2012) showed a relatively high but insignificant correlation ($r= 0.505$), but in 2010 low positive correlations were found. Zinc contents were positively and significantly correlated with Fe, Ni and Co (un-fractionated sediment Zn-Mg $r = 0.474$, $P=.01$; Zn-Fe $r = 0.492$, $P=.01$; Zn-Ni $r = 0.435$, $P=.05$; in less than 63 μ m grain size Zn-Mg $r = 0.613$ $P=.01$; Zn-Co $r = 0.520$ $P=.01$; Zn-Ni $r = 0.649$ $P=.01$). Cadmium in un-fractionated sediments was also significantly correlated with Silver ($r = 0.703$, $P=.05$). In 2010, both Zn contents in both sediment portions were significant correlation, but with less strong correlations in 2012. Other correlations were not provided due to lack of sediment characteristics data.

The sediment enrichment factor (SEF) and geo-accumulation index (I_{geo}) were applied to evaluate the degree of Cd and Zn pollution. SEF is defined as: $SEF = [(X/Al)_{\text{sediment}}]/[(X/Al)_{\text{crust}}]$, where (X/Al or Fe) is the ratio of Zn or Cd to aluminum and iron. The average aluminum content in the earth's crust was excerpted from the data published by Taylor (1964) and a mean Al content (58,732 μ g/g dry wt.) was calculated from monthly lake sediment data of 1994/5 monthly. Baseline values of Fe were derived from recent 2012 data (60,800 μ g/g for <63 μ m grain size fraction and 49,900 μ g/g for un-fractionated surficial lake sediment) and others are the average shale value of Turekian and Wedepohl, (1961) and crustal Fe value (Taylor, 1964).

When the EF of a metal is greater than 1, the metal in the sediment originates from man-made activities, and vice versa. The SEF value can be classified into 7 categories (Birth, 2003): no enrichment for $EF < 1$, minor for $EF < 3$, moderate for $EF = 3-5$, moderately severe for $EF = 5-10$, severe for $EF = 10-25$, very severe for $EF = 25-50$, and extremely severe for $EF > 50$.

The I_{geo} is defined as: $I_{geo} = \log_2 (C_n/1.5B_n)$ (Muller, 1969), where C_n is the measured content of Cd, and B_n is the background content of Cd (0.2 μ g/g and Zn (70 μ g/g) in the average shale. According to Muller (1969) the I_{geo} classes of pollution intensity are as follows: (class 0: $I_{geo} = < 0$ (none), class 1: $I_{geo} = 0-1$ (none to medium), class 2: $I_{geo} = 1-2$ (moderate), class 3: $I_{geo} = 2-3$ (moderately to strong), class 4: $I_{geo} = 3-4$ (strongly polluted), class 5: $I_{geo} = 4-5$ (strong to very strong), and class 6: $I_{geo} > 5$ (very strong). The sediment enrichment factors and geo-accumulation index values of Zn and Cd are shown in Figures 4a to 7b (Supplementary information). Most of the sediment I_{geo} index values were not calculated due to the low contents in most of the <63 μ m grain size fraction during the surveys (Figs. 4a & 4b), but site 8 sites had Cd I_{geo} values above 1. The sediments are considered unpolluted with respect to surficial Zn contents and unpolluted to moderately polluted with respect to Cd at the 8 sites. However, X the SEF values Cd (Figs. 6a-b) in both sediments shows low decreasing and moderate enrichments in 2012 (mostly SEF below 4) from 2010 data (mostly below SEF of 20). Figure 5 show much higher (between 5 and 25) Zn SEF's in the < 63 μ m grain size fraction (2010 & 2012 data) using Al as a baseline compared to Fe. The Zn SEF's in both were similar to values calculated for 1994/5 data, when different values of baseline Al and Fe were used (Figs.

7a-7c), with most SEF values below 4 (moderate enrichments). Zn SEF's were above this level at Sites LS_37, LS_12, and LS_31.

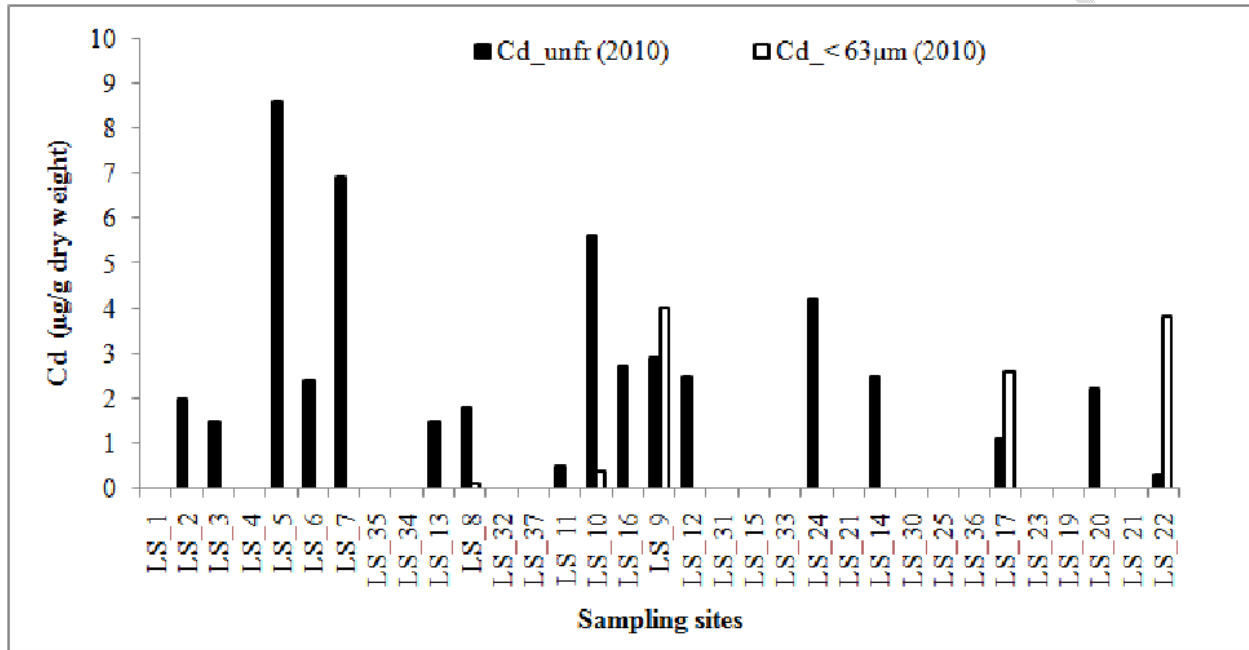


Fig. 3a Cadmium concentration in un-fractionated (unfr) and <63µm grain size surficial sediments (2010 data) from Nyanza gulf.

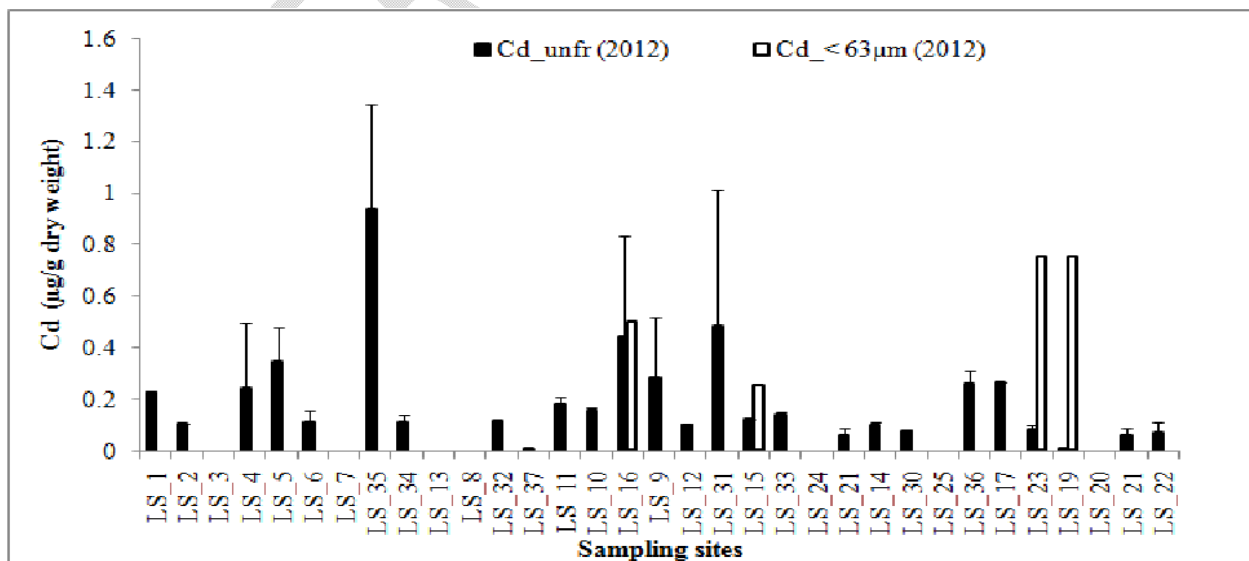


Fig. 3b Cadmium concentration in un-fractionated (unfr) and <63µm grain size surficial sediments (2012 data) from Nyanza gulf

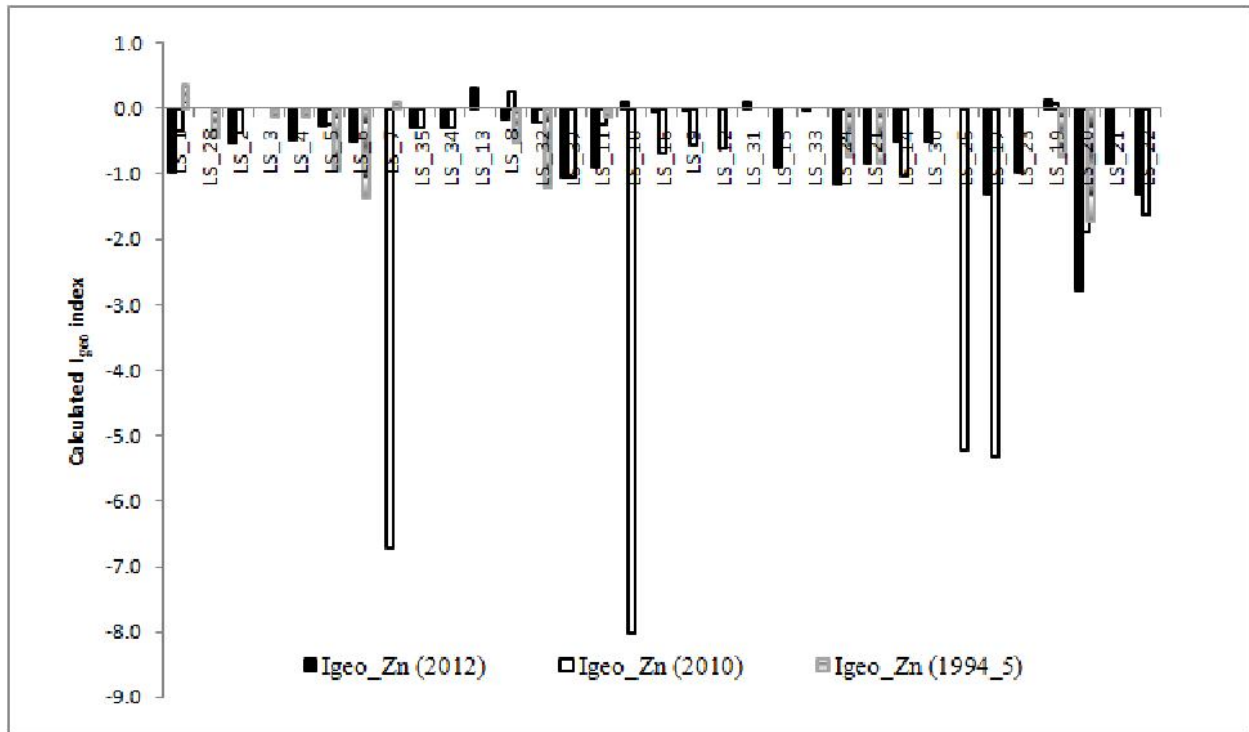


Fig. 4a. Sediment geo-accumulation index (Igeo) values for Zn in < 63µm grain size fraction of the surficial sediments (2012, 2010 & 1994_5 data) in Nyanza gulf.

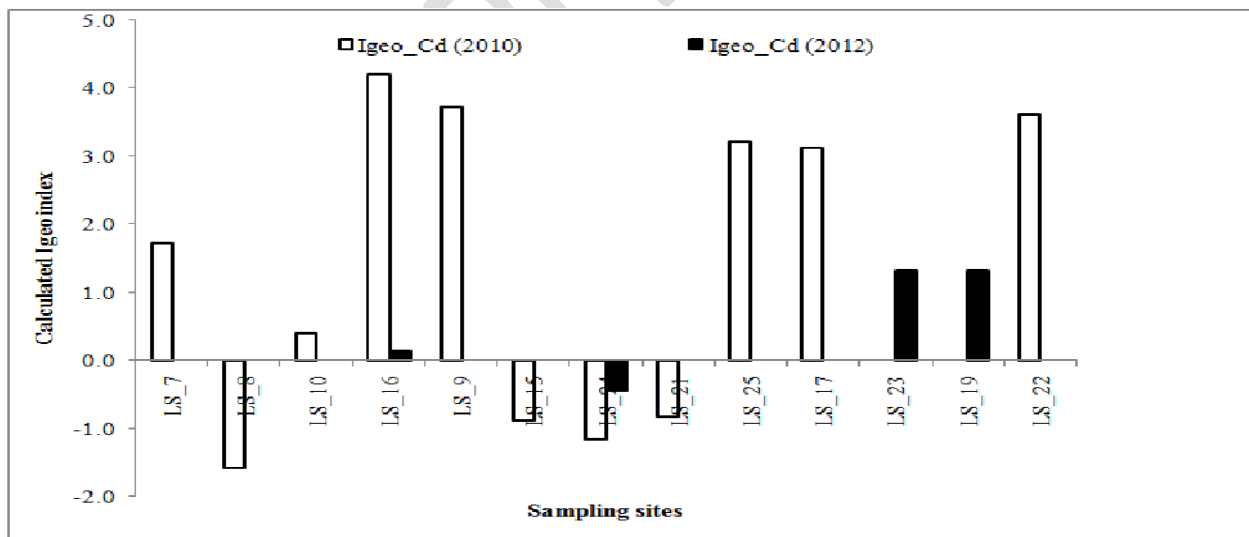


Fig. 4b. Sediment geo-accumulation index (Igeo) values for Cd in < 63µm grain size fraction of the surficial sediments (2012, 2010 & 1994_5 data) in Nyanza gulf.

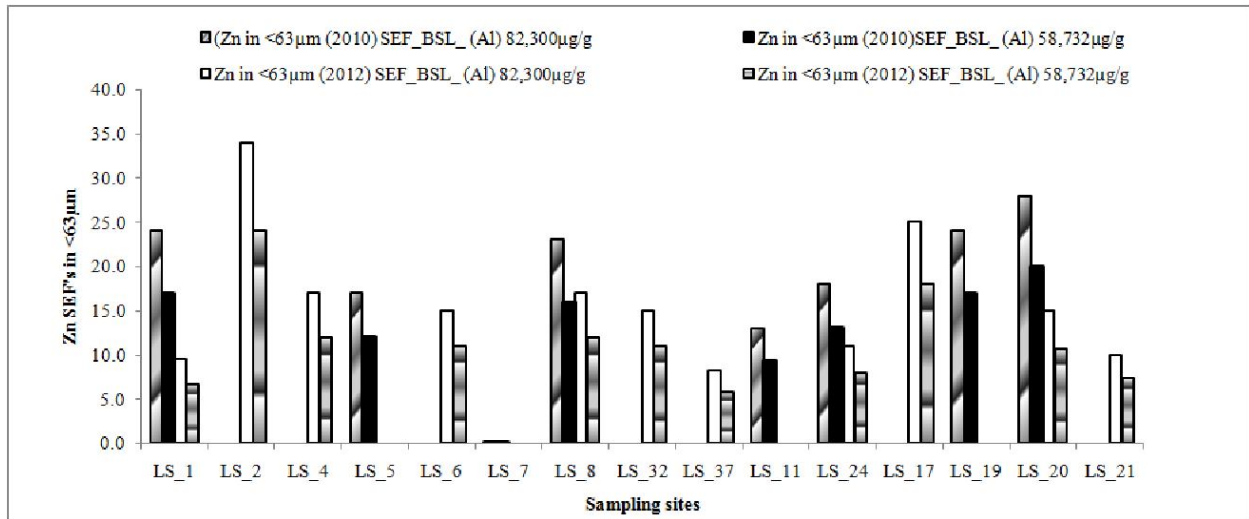


Fig. 5. The calculated SEF for Zn in <63µm grain size fraction of surficial sediments (2012 & 2010 data) using Al baseline values (BSL_Al=82,300µg/g &BSL_Al=58,732µg/g).

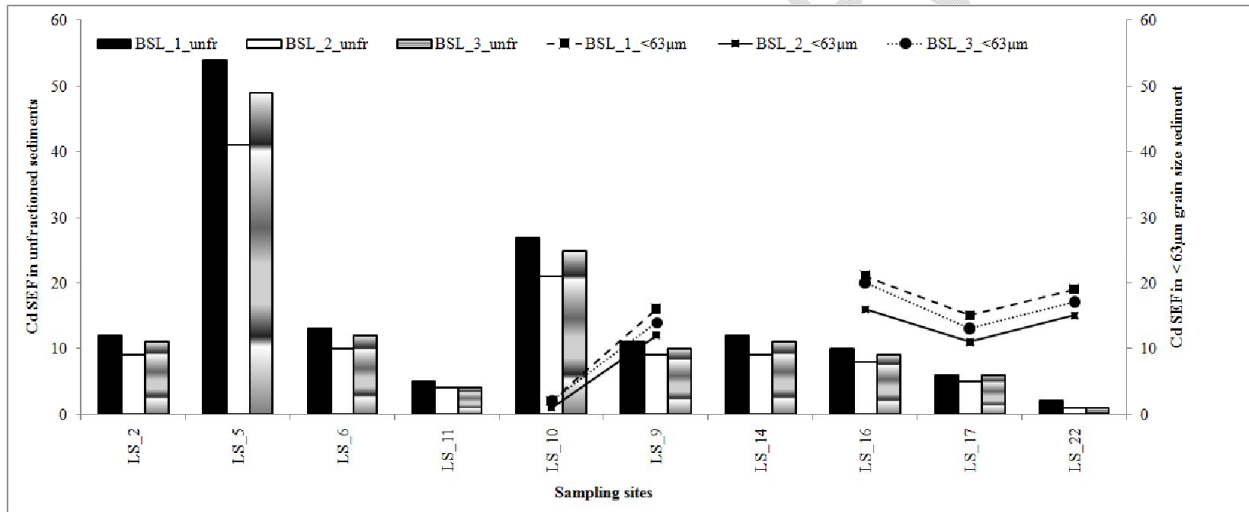


Fig. 6a. The calculated SEF for Cd in un-fractionated (unfr) and <63µm grain size fraction of surficial sediments (2010) using Fe as baseline values (BSL_1=60.800 & 49,900µg/g for Fe in <63µm & un-fractionated sediments respectively; BSL_2=46,700 µg/g; BSL_3=56,000 µg/g).

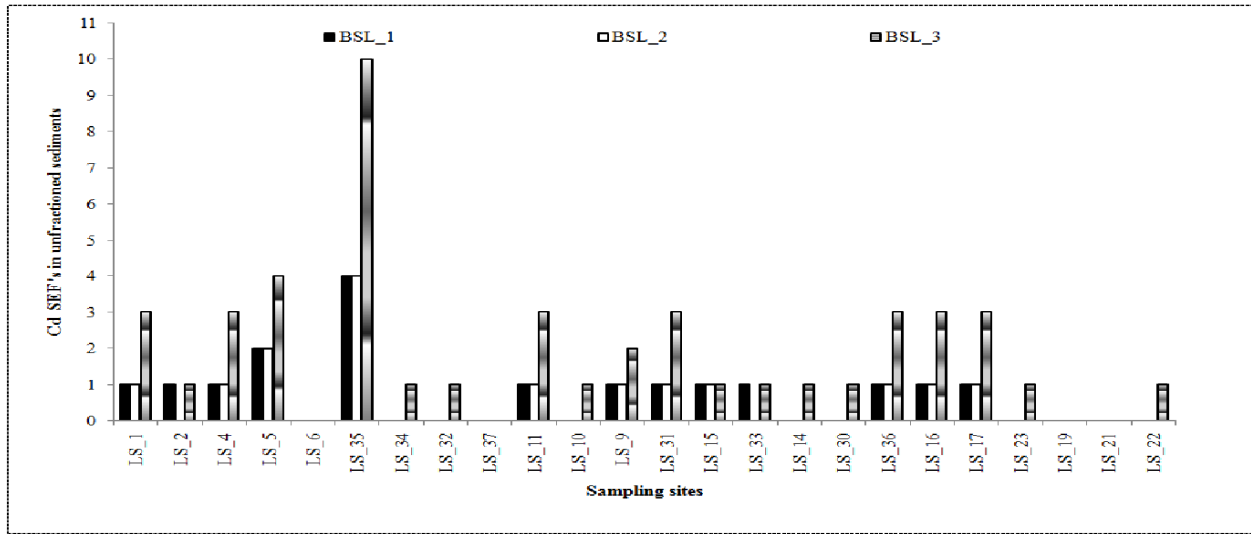


Fig. 6b. The calculated SEF for Cd in un-fractionated surficial sediments (2012) using Fe as baseline values (BSL_1=49,900; BSL_2=46,700 $\mu\text{g/g}$; BSL_3=56,000 $\mu\text{g/g}$).

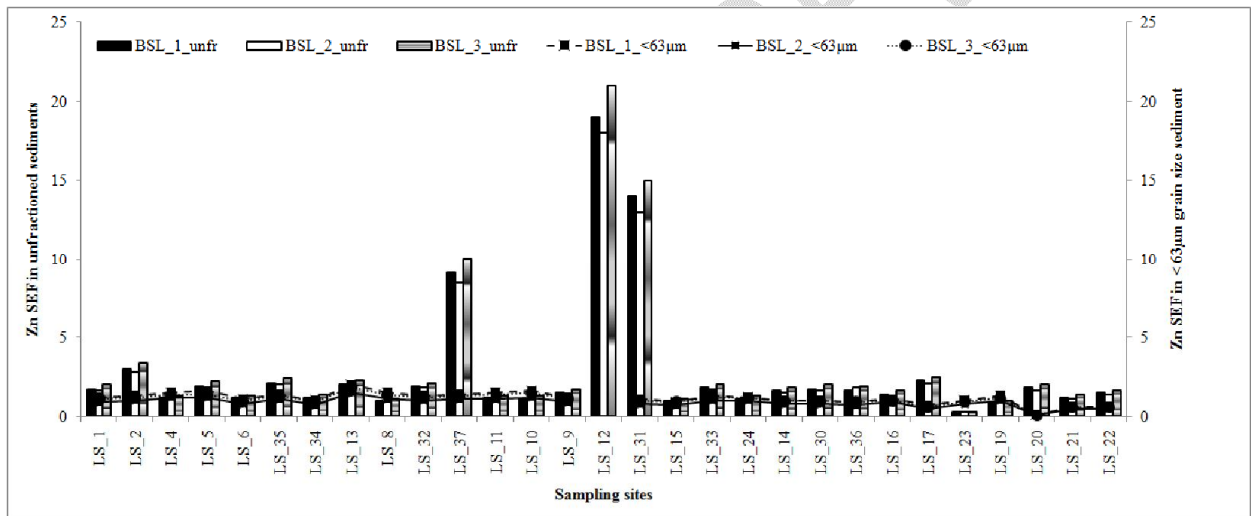


Fig. 7a. The calculated SEF for Zn in un-fractionated (unfr) and $<63\mu\text{m}$ grain size fraction of surficial sediments (2012 data) using Fe as baseline values (BSL_1= 60,800 & 49,900 $\mu\text{g/g}$ for Fe in $<63\mu\text{m}$ & un-fractionated sediments respectively; BSL_2=46,700 $\mu\text{g/g}$; BSL_3=56,000 $\mu\text{g/g}$).

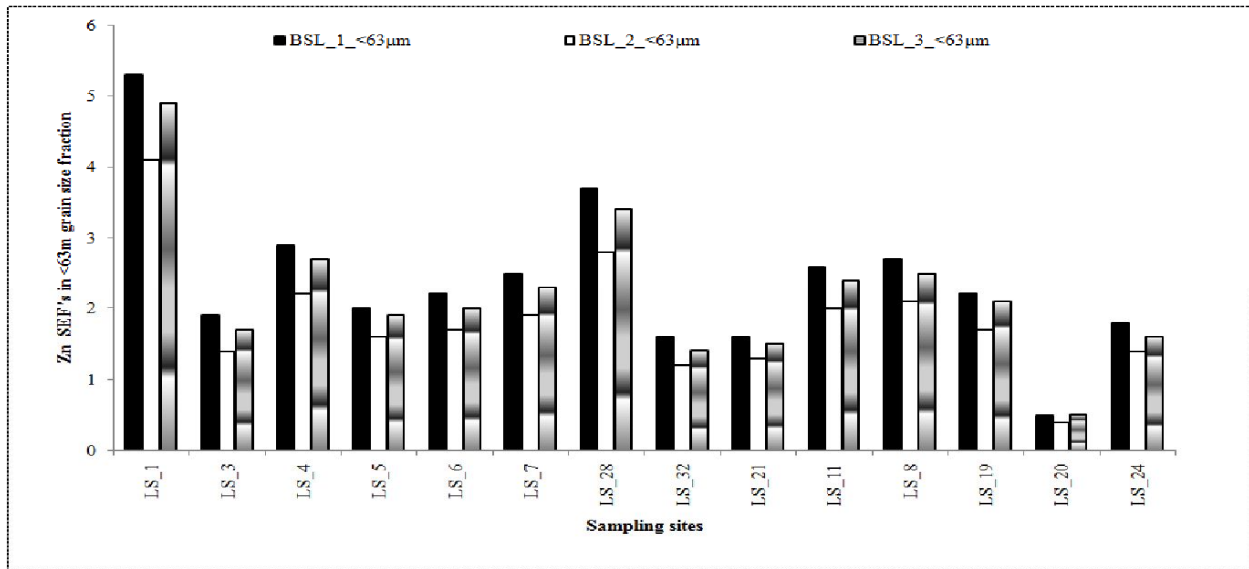


Fig. 7b. The calculated SEF for Zn in <math><63\mu\text{m}</math> grain size fraction of surficial sediments (1994/95 data) using Fe as baseline values (BSL_1=$60,800\mu\text{g/g}$; BSL_2=$46,700\mu\text{g/g}$; BSL_3=$56,000\mu\text{g/g}$).

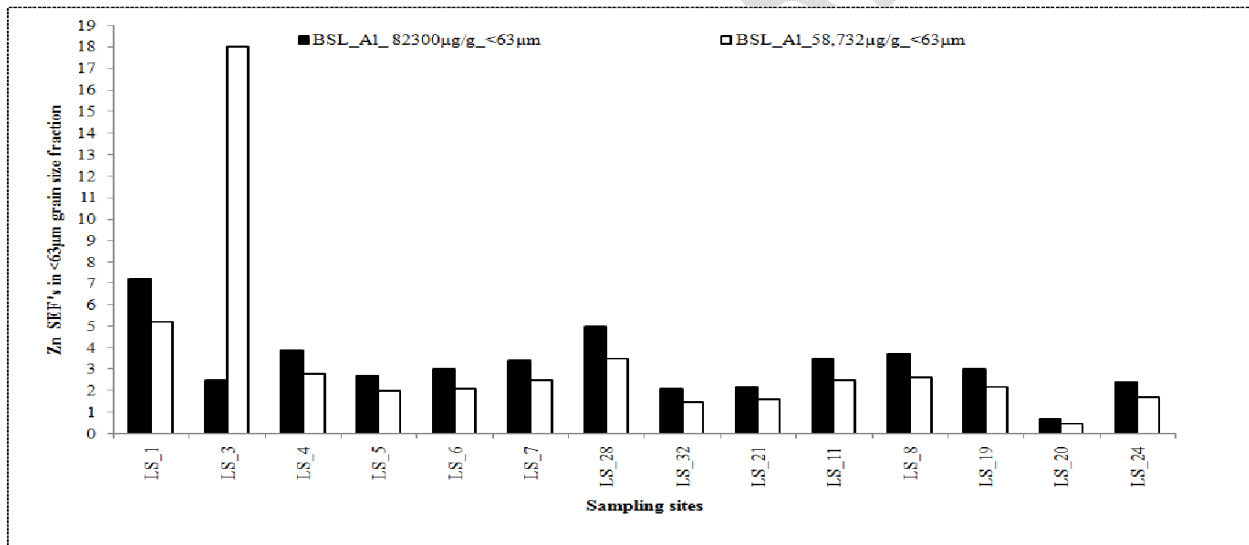


Fig. 7c. The calculated SEF for Zn in <math><63\mu\text{m}</math> grain size fraction of surficial sediments (1994/95 data) using Al ($82,300\mu\text{g/g}$ and $58,732\mu\text{g/g}$) as a baseline value

Table 1. The physico-chemical conditions in surface and above bottom lake waters during the 2012 survey (range values).

	Gulf sites	Main lake sites
pH (surface)	7.60 - 8.51	7.59 – 8.26
(bottom)	7.37 – 8.50	7.37 – 8.05
D.O (mg/l) (surface)	5.07 – 11.12	6.85 – 10.13
(bottom)	4.75 – 8.59	3.45 – 9.71
Temperature °C (surface)	23.87 – 25.86	25.15 – 25.93
(bottom)	23.40 – 25.22	23.02 – 24.95
Conductivity mS/cm (surface)	0.12 – 0.18	0.11 – 0.12
(bottom)	0.13 – 0.23	0.10 – 0.18
Total alkalinity (mgCaCO ₃ /l) (surface)	40 - 194	18 - 60
Hardness (mg/l) (surface)	32 - 80	26 - 28
Secchi depth (m)	0.22 – 0.9	0.2 – 3.2
Water depth (m)	2 - 20	1.4-54

Table 2. Mean (\pm standard deviation) Zn concentration ($\mu\text{g/g}$ dry weight) in surficial lake sediments in different gulf and main lake zones, during 2010 and 2012 sampling (n=northern; s= southern part of the main lake).

		Lake zones and sites			
		Zone I	Zone II	Zone III_s	Zone III_n
2012	Fraction				
	Un-fractioned	144(\pm 56)	97(\pm 29)	106(\pm 67)	134(\pm 49)
	< 63 μm fraction	83(\pm 24)	82(\pm 24)	66(\pm 26)	58(\pm 42)
	No. of sampled sites	8	12	4	4
2010	Un-fractioned	80.1(\pm 48.3)	74.1(\pm 25.4)	44.7(\pm 25.3)	47.8(\pm 32.6)
	< 63 μm fraction	43.6(\pm 56.4)	69.5(\pm 38.4)	17.6(\pm 31.6)	58.2(\pm 46.7)
	No. of sampled sites	14	12	8	6

Table 3. Mean (\pm standard deviation) Zn concentration ($\mu\text{g/g}$ dry weight) in surficial lake sediments at different site sampling depths of the gulf and main lake zones, during 2010 and 2012 sampling (n=northern; s= southern part of the main lake).

	Water depths at sampling sites		
	<5m	5m-10m	>10m
Sediment fraction in the Gulf zones (2012)			
Un-fractioned	125(\pm 48)	88(\pm 39)	115(\pm 25)
< 63 μm fraction	88(\pm 26)	73(\pm 21)	80(\pm 32)
No. of sampled sites	10	7	3
Sediment fraction in the main lake zones (2012)			
Un-fractioned	150(\pm 46)	85(\pm 97)	114(\pm 42)
< 63 μm fraction	39(\pm 22)	54(\pm 17)	90(\pm 33)
No. of sampled sites	3	2	3
Sediment fraction in the Gulf zones (2010)			
Un-fractioned	74(\pm 46)	85(\pm 6)	91.8
< 63 μm fraction	37(\pm 44)	91(\pm 31)	52
No. of sampled sites	9	3	1
Sediment fraction in the main lake zones (2010)			
Un-fractioned	41(\pm 43)	33(\pm 13)	70(\pm 13)
< 63 μm fraction	62(\pm 39)	1.3(\pm 1.8)	89(\pm 33)
No. of sampled sites	2	3	2

Table 4. Mean (\pm standard deviation) Cd concentration ($\mu\text{g/g}$ dry weight) in surficial lake sediments in different gulf and main lake zones, during 2010 and 2012 sampling (n=northern; s= southern part of the main lake).

		Lake zones and sites			
		Zone I	Zone II	Zone III_s	Zone III_n
2012	Fraction				
	Un-fractioned	0.294(\pm 0.317)	0.158(\pm 0.184)	0.261(\pm 0.202)	0.034(\pm 0.038)
	< 63 μm fraction nd-0.75	nd	nd-0.25		nd-0.75
	No. of sampled sites	8	12	4	4
2010	Fraction				
	Un-fractioned	2.72(\pm 3.17)	3.0(\pm 3.3)	0.95(\pm 1.67)	0.83(\pm 1.76)
	< 63 μm fraction nd-3.8	nd-1	nd-4	nd-5.6	nd-3.8
	No. of sampled sites	14	12	8	6

Table 5. Mean (\pm standard deviation) Cd concentration ($\mu\text{g/g}$ dry weight) in surficial lake sediments at different site sampling depths of the gulf and main lake zones, during 2010 and 2012 sampling (n=northern; s= southern part of the main lake).

	Water depths at sampling sites		
	<5m	5m-10m	>10m
Sediment fraction in the Gulf and main lake zones (2012)			
Un-fractioned	0.196(\pm 0.123)	0.102(\pm 0.019)	0.503(\pm 0.478)
< 63 μm fraction	nd	nd-0.25	nd
No. of sampled sites	13	9	6
Sediment fraction in the Gulf and main lake zones (2010)			
Un-fractioned	4.4(\pm 3.3)	4.3(\pm 3.0)	2.5(\pm 0.7)
< 63 μm fraction	nd-4	nd-2.8	nd-5.6
No. of sampled sites	11	6	3

Table 6. Pearson correlations (r) between Zn and Cd and sediment characteristics.

	Un-fractioned sediment (n=30)		<63µm grain size fraction (n=31)	
	Zn	Cd	<Zn	<Cd
2012				
%OM	-0.125	0.253	0.089	-
%CO ₃	0.104	0.130	-0.055	-
%H ₂ O	-0.239	0.028	0.452*	-
<Cd	-	-	0.106	1.000
<Zn	0.137	0.350	1.000	-
2010				
Zn	1.000	-0.484	0.576*	-
<Cd	-	-0.442	0.058	1.000
<Zn	0.576*	-	1.000	0.058

(** and * = r significant at $P=.01$, and $.05$, two tail test); <Cd and <Zn are Cd and Zn contents in <63µm grain size fraction.)

4. DISCUSSION

The changes in sediment Zn and Cd concentrations within the Nyanza Gulf are shown in Table 7 for the surveys conducted from the 1980's to 2012. The concentrations of Zn and Cd in the Nyanza Gulf waters of Lake Victoria show a similar range of concentration (nd to 0.06mg/L Cd, nd to 219.5mg/L Zn), but much higher levels were noted in stream and mine wastes waters, and in 2010 survey. Zn is an essential element, but high dissolved concentrations can have adverse effects on biota, hence the development of sediment quality guidelines for the protection of aquatic life. The consensus based sediment quality threshold effect concentration values (MacDonald et al., 2000, and Burton, 1991, 2002) of Zn, were exceeded by only 4% of the samples. The highest total Zn concentration recorded in surface waters was 4.00 mg/l, although the more bioavailable dissolved form was not determined. The sub-surface lake water is often reported to be, well oxygenated and sometimes to even deeper depths (Table 1), with high near neutral pH. Such conditions can significantly influence the controls on the chemical equilibria and the chemical elements behavior, including heavy metal cations. Cationic elements will therefore tend to be adsorbed onto surfaces of the insoluble hydroxides and oxide particles. This scenario explains the relatively high contents in the unfiltered lake water compared to the more bioavailable dissolved forms. Adsorption of Cd concentrations is variable, and variations in the range of 1-90% adsorbed Cd are to be expected under conditions typical of many freshwaters (Laxen, 1984). This can be the reason why dissolved and total Cd concentrations in the lake are normally very low and undetectable in some cases, albeit the much higher and highly variable sediment Cd contents found during different surveys. Chemical exchanges at the sediment-water interface and differences in the composition of deposited sediments and sediment redistribution through resuspension in shallow areas, has a great potential in influencing the sediment metal contents. The specific area is a key particle property which controls adsorption capacity and is inversely proportional to particle size and decrease over three orders of magnitude from clay sized particles to sand grains (Chapman, 1992). It is therefore accepted that X fine particles are the richest in trace elements (Horowitz, 1991, Chapman, 1992). Increased binding of complexed and adsorbed particulate Cd is possible in sediments which act as the final repository sites of metal loads from inflowing waste discharges and other surface eroded deposits, together with the increasing eutrophic conditions described by Sitoki et al., (2010), Lungaiya et al., (2001), and Hecky, et al., (2010). Although the fractionation evaluations were not done during the two surveys, in previous speciation studies (Mwamburi, 2013, Ongeru et al., 2015), high bioavailable forms of Cd have been reported in surficial sediments, and hence there is reason to be concerned about the high enrichments in sediments, as it is a potential ecological risk to benthic biota. The adsorption process in lake water of high dissolved oxygen and pH, together with sedimentation is an important control to availability of metal ions. Biosorption has also been evaluated experimentally as a possible means of metal removal in the lake. Water hyacinth is naturally now available in the lake, and according to Anzeze et al., (2014a, 2014b) it could offer alternative biomass for X removal of aqueous ions of Cd^{2+} and Zn^{2+} , due to its high adsorption capacity. Therefore reduction of sources of metal ions from waste water can be enhanced by aquatic macrophytes, and hence the need to sustain the lakeshore and wetland vegetation.

The cadmium total concentration in lake water were below detection levels (n=18) and hence water did not exceed the health guideline value of 0.002mg/L (NHMRC NRMCC, 2011), 0.005mg/L, Cd (WHO, 1984) and 0.01mg/L, Cd (EMCA, 2006) in drinking water. The mean (\pm standard deviation) total Zn concentration in surface lake water was 1.96 ± 0.24 mg/L, and

exceeded the EMCA (2006) recommended level of 1.5 mg/L for aesthetic quality. However, from the 1994/5 data (excluding

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Table 7. Changes in sedimentary Cd and Zn concentrations ($\mu\text{g/g}$ dry wt. mean \pm sd and mean ranges) at selected sites in the Nyanza gulf of L. Victoria from different surveys between 1985 and 2012.

Cd

Sites	2012 (<63 μm)	2012 (UF)	2010 (<63 μm)	2010 (UF)	1994/5 ^a	1985 ^b (mg/kg dry wt.)
LS_1	nd	0.226 \pm 0.004	nd	nd	nd	0.61 \pm 0.0, 0.99 \pm 0.03, nd,
LS_5	nd	0.345 \pm 0.134	-	8.60	nd	0.57 \pm 0.14
LS_7	nd	-	1.0	6.9	nd	0.50 \pm 0.07
LS_24	nd	-	nd	4.2	nd	0.83 \pm 0.15
LS_11	nd	0.180 \pm 0.030	nd	0.5	nd	0.57 \pm 0.07
LS_14	nd	0.097 \pm 0.011	nd	2.5	-	nd
LS_33	nd	0.135 \pm 0.013	-	-	nd	-

Zn

Sites	2012 (<63 μm)	2012 (UF)	2010 (<63 μm)	2010 (UF)	1994/5 ^a	1985 ^b (mg/kg dry wt.)
LS_1	53.3	135	nd	nd	136.4	3.40 \pm 0.87
LS_5	87.5	120	-	8.6	54.4	142 \pm 1.9
LS_7	-	-	1.0	42.1	113.6	98.74 \pm 1.40
LS_24	47.3	43.8	77.6	91.5	63.6	122 \pm 0.9
LS_11	56.3	104	89.4	95.4	95.5	157 \pm 30

LS_14	74.0	62.3	52.0	91.8	-	-
LS_33	104.2	126	-	-	-	101±0.4

Reported concentrations of Cd and Zn around Nyanza gulf of Lake Victoria

WinamGulf water (Cd = 0.02±0.004-0.06±0.009mg/l), sediments (Cd = 0.05±0.03-0.21±0.05mg/kg), Oyoo-Okothet *al.*, (2010).

WinamGulf (dissolved Cd = nd-5.54µg/l; dissolved Zn = 14.5-55.9 µg/l), sediments (Zn = 65.0-146.5µg/g; Cd = 0.25-1.08µg/g), Ochienget *al.*, 2008.

WinamGulf water (dissolved Cd = nd-8µg/l; dissolved Zn = 25-219.5µg/l), sediments (Cd = nd-1.78µg/g; Zn = 23.39-350.8µg/g), Lalahet *al.*, 2008.

WinamRiver water (Cd = <1.798µg/l, Zn = 4.37-11.6µg/l), sediments (Cd = 0.19-1.91x10³ µg/kg, Zn = 36.2-443x10³ µg/kg) Ongeriet *al.*, 2009.

WinamGulf water (Zn = 0.036 – 0.076 ppm, Cd = nd); algae (Zn = 0.055 – 0.110 ppm; Cd = nd – 0.013 ppm), sediments Zn = 0.445 – 2.248 ppm; Cd = nd) Ogoyiet *al.*, 2011.

WinamGulf water (Zn = 0.14±0.00 mg/l, Cd = nd - 0.02±0.00 mg/l); sediments Zn = 36.7±1.53 - 277±1.53 mg/kg; Cd = nd - 3.3±0.50 mg/kg) Muindeet *al.*, 2014

WinamGulf water Cd (0.01-0.02, mean 0.01 mg/l), sediments Cd (0.4-2.8 mg/kg), Shitsama (1999).

WinamGulf sediments Cd (0.0-1.0 mg/kg), Wandiga&Onyari (1987).

Soils and water around Au mining areas (soils Cd = 4.5 - 570 mg/kg; water (Cd = 1.5 - 10.5µg/l) Ngureet *al.*, 2014.

Soils around 4 major urban areas of Nyanza gulf (soils Cd = 0.52±0.05 – 1.82±0.08 µg/g); water Cd = 0.03±0.01 – 0.12±0.03 µg/l) Oyoo-Okothet *al.*, 2013.

Au mine ores and sediment (Zn = 29.90 - 63,210 mg/kg), mine waste waters (Zn = 33.69±4.29 - 683.15±32.93 µg/l) Odumet *al.*, 2011a,b.

UF=un-fractioned sediment; <63µm = sediment grain size analyzed; a=Mwamburi&Oloo 1996/7; b= Wandiga&Onyari 1987.

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the southern section of main lake in Kenya part), Cd concentrations in lake have been relatively low, with much higher contents of Zn, ranging from 0.008mg/L to 0.07 mg/l in surface and bottom water. There is no health based guideline value proposed for Zn in drinking water, but in most organizations , guidelines based on aesthetic considerations exist. Zinc concentration in drinking water should not be exceed a value of 3mg/L Zn, as recommended for Australian waters (NHMRC NRMCC, 2011) and 0.001mg/L Zn for WHO (1984). Although Zn is normally an essential element, excessive exposure levels in the environment and aquatic ecosystems are of concern.

“Inefficient production and recycling operations release considerable amounts of lead and cadmium with both environmental and human health impacts” (UNEP, 2010). “The weathering of rocks releases cadmium to soils and aquatic systems and plays a significant role in the global cadmium cycle. Weathering and erosion result in the transport by rivers of large quantities of cadmium to the world's oceans” (UNEP, 2010). “Limits on the content of cadmium in phosphate fertilizers has been established in a number of countries. The aim of these restrictions is generally to limit the supply of cadmium to agricultural soils” (UNEP, 2010). “The toxicity of chemicals in sediments is influenced by the extent to chemicals bind to the sediment. It is shown that acid volatile sulfide (AVS) is the sediment phase that determines the LC50 for cadmium in the marine sediments tested. Although it is well known that metals can form insoluble sulfides, it apparently has not been recognized that AVS is a reactive pool of solid phase sulfide that is available to bind with metals. Because other toxic metals also form insoluble sulfides, it is likely that AVS is important in determining their toxicity in sediments as well. Most freshwater and marine sediments contain sufficient acid volatile sulfide for this phase to be the predominant determinant of toxicity” (DiToro et al., 1990)

“Cadmium enters aquatic systems through aerial deposition or runoff and accumulates in bed sediments by association with particulate matter, such as organic matter and iron and manganese hydroxides, or by precipitating out of solution with carbonate or sulfide” (Landrum and Robbins, 1990, X Burton, 1992). Clay minerals, organic matter, and oxides of Fe and Mn are important geochemical substrates in providing sediments with the capacity to sequester and retain trace elements. In this way, metals incorporated in the crystalline mineral structure, adsorbed on fine-grained sediments, complexed with different organic substances, co-precipitated with hydrous Fe and Mn oxides and carbonates accumulate in the sediments. Besides concentrating inorganic and organic contaminants, increasing inputs of suspended and re-suspended sediments also act as a physical pollutant, impairing the water quality. Sediments, therefore, act as an important route of exposure for aquatic organisms. Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for Cd (Table 7) can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to Cd in sediments (CCME,1999).

Metals are accumulated by filter feeding organisms via water, ingestion of suspended sediments or food. A substantial proportion of the total cadmium in river and lake water will usually be present as the free cadmium ion, and this proportion will be larger the lower the pH value and the lower the proportion of sewage effluent present in the water (Gardiner, 1974). The concentrations of cadmium that result in acute or chronic toxicity vary over several orders of magnitude, with certain freshwater fish and invertebrates being the most sensitive (Wright and Welbourn, 1994). In freshwater spiked-sediment toxicity tests, reproduction of the burrowing

oligochaete worm *Tubifex tubifex* was adversely affected when the concentration of Cd (i.e., 12 mg·kg⁻¹) was greater than the freshwater PEL and the total organic carbon (TOC) content was 1%. At similar concentrations of Cd, but with a TOC content of 12%, no adverse effects were observed (Day et al., 1994). These results suggest that organic matter may modify the toxicity of Cd to freshwater benthic organisms. Other freshwater spiked-sediment toxicity tests did not demonstrate adverse effects of Cd at concentrations known to occur in aquatic environments (Environment Canada, 1997). Fish sampled along four sites in Lake Victoria, Kenya differing in metal contamination, accumulated higher Cd, Cr and Zn in the whole body and in the gut of parasitized fish compared to non-parasitized fish, while Cu was depleted in parasitized fish. Generally, for both non-parasitized and parasitized fish, Cd, Cr and Zn partitioned in the cytosolic fractions and Cu in the particulate fraction. Metal concentrations in organelles within the particulate fractions of the non-parasitized fish were statistically similar except for Cd in the lysosome, while in the parasitized fish, Cd, Cr and Zn were accumulated more by the lysosome and microsomes (Oyoo-Okoth et al., 2012a). X The study revealed specific binding of metals to potentially sensitive sub-cellular fractions in fish in the presence of parasites, suggesting interference with metal detoxification, and potentially affecting the health status of fish hosts in Lake Victoria (Oyoo-Okoth et al., 2012a).

The bioavailability and toxicity of zinc contaminated sediments (low 44±5, medium 526±41, high 961±38µg/g dry mass) were investigated in laboratory microcosms for 28 days by examining *H. australis* exposure-dose-response relationships (Wadige et al., 2014) Based on exposure-dose analysis, the freshwater bivalve *Hyridella australis* partially regulates zinc uptake and weakly exhibits bioavailability of zinc in freshwater environments, however, exposure-response analysis shows zinc induced toxicological effects, suggesting the potential of this organism as a biomonitor for zinc in heavily contaminated freshwater environments (Wadige et al., 2014). In L. Erie, the Cd and Zn levels in burrowing mayflies, *Hexagenia* were on average approximately 4 and 2 times greater, respectively, than sediment levels, and the Cd concentrations in the sediments exceeded the threshold effect level at 27 of 28 sites and exceeded the probable effect level at 9 of 28 sites. Spatial representation of heavy metal concentrations in mayflies exhibited a similar pattern to the spatial distribution of heavy metals and organic matter in the sediments with higher concentrations of metals found in mayflies residing in the central deeper region of the western basin (Opfer et al., 2011). According to Muysen et al., (2006), an integrated response of *Daphnia magna* following chronic zinc exposure for 21 days to dissolved Zn concentrations up to 340µg/L, found X that after 1 week, only 7% of the organisms exposed to 340µg/L survived. Body Zn contents of these organisms were 281±76µg/g dry weight and a 37% decrease of the Ca contents was observed. This suggests a competitive effect of Zn on Ca uptake (Muysen et al., 2006). In a cadmium spiked suspended sediment experiment (19 and 93µg/g Cd dry mass), most cadmium was desorbed from sediments and cadmium concentrations in oysters, *Saccostrea glomerata* were significantly related to dissolved cadmium concentrations (4–21µg/L) in the overlying water (Schmitz et al., 2015).

The significant exposure-dose-response relationship for *A. trapezia* exposed to cadmium enriched sediments (sediments spiked with 10µg/g and 50µg/g Cd dry mass) indicates that elevated sediment cadmium concentrations have the potential to lead to increased biologically active cadmium burdens and impairment of individual *A. trapezia* at cellular and subcellular levels. (Taylor and Maher, 2012). Results of both marine and freshwater spiked-sediment toxicity tests indicate that concentrations of Cd that are associated with adverse effects are consistently above the ISQGs (Table8), confirming that these guidelines represent

concentrations below which adverse biological effects will rarely occur. Furthermore, these studies provide additional evidence that toxic levels of Cd in sediments are similar to the PELs, confirming that adverse effects are more likely to be observed when concentrations of Cd exceed the PELs. The ISQGs and PELs for Cd (Table 8) are therefore expected to be valuable tools for assessing the ecotoxicological relevance of concentrations of Cd in sediments. (CCME, 1999). Other studies elsewhere have reported decreasing trends in metals in lake sediments (Marvin et al., 2003). Concentrations of dissolved forms of cadmium are normally very low in the lake water, but detectable levels were found in the solid phase during this study and were also reported in different sediments studies, indicating that the bioavailable forms in sediments are relatively high and are a cause of concern as regards the protection of aquatic biota.

Recent concerns have also been raised about chemicals accumulation and enrichment in marine sediments from marine aquaculture activities where metals, such as Cu and Zn were identified as being of significance. However, this was not part of the study, and no information has been provided for lakes and ponds sediments, where aquaculture activities can be regarded as important sources, of metals from wasted un-utilised feeds and antifoulants, especially around the farms, in the long-term.

Table 8. Evaluation of sediment quality using the available threshold, mid-range and extreme effect values (values given as % of samples exceeding the value for Cd and Zn).

	Threshold effect sediment quality guideline values (mg/kg)							
	2012<63µm		2012unfr		2010<63µm		2010unfr	
	Cd	Zn	Cd	Zn	Cd	Zn	Cd	Zn
TEL ^a (Cd=0.6, Zn=123) 4.8%		7%	4%	8%	36%	0.3%	10%	51%
ERL ^a (Cd=5)	0%	4%	0%	31%	0.1%	10%	15%	4.8%
LEL ^a (Cd=0.6, Zn=120) 4.8%		7%	0%	8%	14%	0.3%	0%	51%
MET ^a (Cd=0.9, Zn=150)	0%	4%	2%	39%	0.3%	10%	51%	4.8%
CB-TEC ^a (Cd=e0.99, Zn=121)	0%	4%	2%	32%	0.3%	10%	51%	4.8%
EC (TEL) ^b (Cd=1.2, Zn=124)	0%	0%	2%	14%	0.3%	0%	46%	4.8%
NOAA ERL ^c (Cd=1.2, Zn=150) 0%		0%	0%	2%	14%	0.3%	0%	46%
ANZECC ^e (ERL) (Cd=1.5,Zn=200)	0%	0%	0%	14%	0.3%	0%	46%	0%
ANZECC ^e (ISQG_Low(Cd=0.58, Zn=200)	7%			8%		0.3%		51%

2. Mid -range effect sediment quality guideline values (mg/kg)

Cadmium	2012<63µm	2012unfr	2010<63µm	2010unfr
PEL ^a (3.53)	0%	0%	15%	29%
ERM ^a (9)	0%	0%	0%	2.4%
EC (PEL) ^b (4.21)	0%	0%	5%	22%
NOAA (ERM) ^c (9.6)	0%	0%	0%	2.4%
SQAV (PEL)(3.2) ^d	0%	0%	15%	29%

2. Extreme effect sediment quality guideline values (mg/kg)

Cadmium	2012<63µm	2012unfr	2010<63µm	2010unfr
TET ^a (3)	0%	0%	10%	29%
SEL ^a (10)	0%	0%	0%	0%
CB (PEC) ^a (4.98)	0%	0%	5%	15%

TEL^a=threshold effect level; ERL/M^a=effects range low/medium; LEL^a=lowest effect level;CB^a=consensus based; MET^a=minimal effect level; SQAV=sediment quality advisory value; ISQG^d=interim sediment quality guideline; PEC=probable effect concentration; PEL=probable effect level ;SEL=severe effect level; TET=toxic effect threshold; ANZECC 1997^e=Australian and NewZealand Environment and Conservation Council. EC-TEL^b; NOAA-ERL^c; (a=MacDonald *et al.*, 2000; b=Smith *et al.*,1996; c=NOAA 1999 d=Swartz 1999).

5. CONCLUSIONS

The total concentrations of the metals were much higher in the sediments than in the overlying lake waters, as previously found and reported by several other investigations. The mean concentrations of Cd and Zn in the un-fractioned surficial sediments collected in 2010 were found not to be significantly different ($p>0.05$) from those in the less than 63µm grain size fraction. However, during the 2012 survey, mean Zn contents in the un-fractioned sediments were found to be significantly higher ($p<0.05$). About 33% and 25% of the sediments contained much higher amounts of Zn and Cd in the finer sediment fraction in the 2010 survey as compared to 25% and 11% in the 2012 survey.

The 95% confidence limit for the un-fractioned sediment mean Zn exceeded the upper level (Table 8) of no effect concentration (consensus based value), but was still lower than the PEC values. Only 2% of the un-fractioned sediment samples had Cd levels above the threshold effect concentration during the 2012 survey compared to 51 % in 2010, but none exceeded the severe effect level. All sediment Zn concentrations were below the mid-range effect concentration of the sediment quality guideline values, and only 4% (2012) and 10% (2010) of

the finer sediments and 32% (2012) and 4.8% (2010) of the un-fractioned sediments exceeded consensus based threshold effect concentration.

The spatial distribution of Cd and Zn in the surficial sediments shows unpolluted to moderate levels enrichment of Cd and Zn. Cd enrichments were highly variable compared to Zn, which showed a more general uniform trend in most of the gulf areas, but Cd SEF appeared to increase when compared to previous data. A combination of surface erosion and storm waters washout of urban wastes, uncontrolled releases of wastes into surface waters contributes to the surface enrichments of metals in the lake environment, and reduction of these loads will significantly lessen the potential of increased bioavailability and bioaccumulation in the aquatic ecosystem.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

The author hereby declare that no generative artificial intelligence (AI) technologies such as Large Language Models (ChatGPT, COPILOT, ect.) and text - to - image generators have been used during writing or editing of manuscript.

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